FY 2009 Final Report

COASTAL CO_2 MEASUREMENTS AND DATABASES FOR THE NORTH AMERICAN CARBON PROGRAM

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GC05-288	*FY05a (6/1/05-12/31/05)*	*FY06a (1/1/06-12/31/06)*	*FY07a (1/1/07-12/31/07)*	*FY08a (1/1/08-2/28/09)*	**sumFY05a-FY08a (6/1/05-2/29/09)**
PMEL	*76701*	*198120*	*234823*	*113405*	623048
AOML	*40814*	*157722*	*225432*	*40814*	464782
OSU	*29806*	*97814*	*126885*	*58877*	313381
UGA	*30114*	*61828*	*73207*	*41493*	206641
				Total:	1607852

1.0 Summary of Accomplishments (2005–2009)

All major goals of the *Coastal CO_2 Measurements and Databases for the North American Carbon Program* proposal were successfully completed during the period of funding, with several publications completed and several additional ones in various stages of preparation or review. During the funding period, with leveraged funding from NASA and other sources, GCC-supported research activity included large-scale hydrographic surveys of all coasts of the 48 contiguous United States and into Canada and Mexico, deployment of an autonomous pCO_2 system on a National Data Buoy Center mooring off of Georgia (complemented by three more off Mississippi, Washington, and Maine, funded by NOAA/CI, NASA, and NSF, respectively), installation of autonomous underway pCO_2 systems on NOAA research ships, advances in CO_2 mapping and prediction algorithms, and development of an ocean CO_2 database management system.

Large-scale surveys of the North American continental shelf to characterize the spatial variability in carbon cycle and related parameters in coastal regions were successfully completed along the U.S. Pacific, Gulf, and Atlantic coasts in 2007. These surveys were consistent with previous, smaller scale studies showing that spatial heterogeneity in pCO_2 is high along the North American continental margin. At the time of the West Coast Cruise (WCC, May–Jun. 2007), the northern part of the West Coast (British Columbia–Oregon) was a net CO_2 sink while the southern part was a source (California–Baja California). During the Gulf of Mexico and East Coast Cruise (GOMECC, Jul.–Aug. 2007), the regions surveyed were overall net sources of CO_2 to the atmosphere with strong localized sinks near rivers and estuaries. The WCC revealed that water masses undersaturated with respect to the carbonate biomineral, aragonite, are present on the western North American continental shelf from British Columbia to Baja California and reach the surface in northern California during the upwelling season (Feely et al., 2008a). The cruise dataset also facilitated the development of algorithms to hindcast carbonate saturation states based on more widely available, proxy hydrographic variables (Feely et al., 2008b; Juranek et al., accepted).

High-resolution seawater and atmospheric pCO_2 data have been collected from the moored autonomous pCO_2 ($MAPCO_2$) system deployed on a NOAA National Data Buoy Center (NDBC) mooring located in the South Atlantic Bight (SAB) off Savannah, Georgia, from 2006 to 2009, revealing interesting inter-annual variability. The moored CO_2 data have been consistent with data from repeated and spatially extensive sampling of CO_2 in the SAB in 2005-2006, showing that this part of the East Coast is a CO_2 sink in the winter, a source in the summer, and a net sink on an annual basis.

Underway pCO_2 measurements also contributed valuable information about coastal CO_2 variability. During the funding period, approximately half a million new pCO_2 observations were made by this team, significantly improving data coverage along North American continental margins. New observations in the Gulf of Mexico (GOM) have been particularly critical for refining our understanding of North American coastal CO_2 exchange fluxes, as the region had been estimated to be a large source of CO_2 in the *First State of the Carbon Cycle Report (SOCCR)* chapter on coastal ocean CO_2 fluxes, but was exceptionally poorly sampled previously. New observations suggest that at least the northern GOM is in fact a net annual CO_2 sink.

Significant strides were made in developing mechanistic prediction algorithms relating pCO_2 in highly dynamic coastal zones to remote sensing products for chlorophyll, sea surface temperature, and wind speed. Incorporation of neural networks to generate self-organizing maps of coherent biogeochemical regions allowed the development of region-specific prediction algorithms for the strongly variable sub-regions along the continental margins. These advances have facilitated the generation of improved annual estimates of air-sea exchange along continental margins, again yielding substantially different results than those in the *SOCCR* coastal synthesis.

Finally, advances in the Ocean Carbon Data Management System (OCDMS) have improved the user interface—for instance, by making it possible to easily select subsets of the CO_2 database for subsequent analysis and visualization. Recent improvements to OCDMS have also proven beneficial to the effort to maintain stringent data quality controls on community CO_2 databases, by identifying out-of-range and duplicate data points. The successes of the OCDMS formed the software basis for later work to support the Surface Ocean CO_2 Atlas (SOCAT) project, an international CO_2 synthesis effort devoted to providing the carbon community with a uniformly formatted, quality controlled global ocean CO_2 database that will drive the subsequent generations of global coastal ocean CO_2 climatologies.

Collectively the work funded by this proposal and synergistic, parallel efforts funded by other agencies has established an important foundation for future coastal carbon cycle studies as well as for an ocean acidification research and monitoring observatory. *These coastal biogeochemical studies continue to reveal unexpected results that highlight the need for a continued observational effort for coastal carbon.* This need is particularly critical and timely in light of the linked carbon cycle problems of ocean acidification and hypoxia that threaten the well-being of the rich coastal ecosystems of North America that provide a variety of socioeconomically important resources to this continent's population.

2.0 Introduction

The continental margins of North America are the primary zone where open ocean, atmospheric, and terrestrial carbon cycles interact, and as such, the large carbon fluxes occurring within or passing through the coastal oceans are of great importance for accurately quantifying the carbon budgets of the bordering open ocean, atmospheric, and terrestrial regions. Prior to the work supported by this grant, air-sea carbon fluxes along the Pacific, Atlantic, and Gulf coasts of North America were so poorly under-sampled that uncertainty remained whether these regions were net sources or sinks for CO_2 (e.g. Doney et al., 2004; Hales et al., 2008a). The only published coastal CO_2 synthesis for North America, undertaken for the *First State of the Carbon Cycle Report*, suggests that North American coastal oceans collectively act as a weak source of 19 ± 22 Tg C yr^{-1} CO_2 to the atmosphere, with the total being the sum of strong CO_2 sources at low latitudes on the Pacific and Atlantic coasts and in the Gulf of Mexico (14 ± 9 Tg C yr^{-1} alone), balanced by strong CO_2 sinks in mid to high latitude Pacific and Atlantic continental margins (Chavez et al., 2007). However, the extreme paucity of observations in regions contributing large magnitude CO_2 fluxes (e.g. Gulf of Mexico, Gulf of Alaska) to this integrated, continent-scale annual flux estimate underlined the uncertainty of these results. The work funded by this proposal significantly improved our ability to robustly estimate continental margin air-sea CO_2 fluxes, in terms of both improved sample coverage along many North American coastlines and significant methodological advances in extrapolation and synthesis techniques for generating CO_2 flux maps.

3.0 Project Objectives

The original objectives delineated in the proposal for the funded work were:

(1) To extract existing coastal data sets from presently existing automated NOAA underway pCO_2 files to build a database of carbon measurements for the purpose of determining U.S. coastal air-sea CO_2 fluxes.

(2) To construct and deploy new automated underway pCO_2 systems for coastal research vessels and autonomous pCO_2 systems for moorings.

(3) To conduct large-scale coastal surveys of pCO_2 and related chemical and hydrographic measurements to determine the spatial scales of CO_2 sources and sinks, and causes thereof, along the East, Gulf, and West Coasts of North America to gain better insight into the infrastructure required to properly develop a long-term monitoring program for the North American Carbon Program (NACP) and for the purpose of designing future process and time-series studies.

(4) To develop a database management system and real-time web access to the data via a Live Access Server of NOAA coastal pCO_2 and related data.

4.0 West Coast, Database, and Mooring Results and Accomplishments (Feely, Sabine, Alin, Hankin, Wanninkhof, Langdon, Zhang, Hales, Cai)

A major accomplishment was the successful completion in 2007 of the first North American Carbon Program (NACP) West Coast Cruise, led by Chief Scientists Richard Feely and Chris Sabine. The 33-day cruise on the R/V *Wecoma* started on May 11 in Newport, Oregon, and ended on June 14, 2007 in San Diego, California. During the cruise, a total of 111 stations along 13 transect lines orthogonal to the coast were sampled, extending from Queen Charlotte Sound, British Columbia, Canada, in the north, to San Lazaro Bay, Baja California, Mexico, in the south (Figure 1). Water samples collected with a 24-bottle rosette at each CTD station were analyzed for salinity, oxygen, nutrients, dissolved inorganic carbon, total alkalinity, dissolved organic matter, colored dissolved organic matter, particulate organic carbon, biogenic silica, and chlorophyll. Underway measurements of atmospheric pCO_2, near-surface seawater pCO_2, and bio-optical properties were also made along the cruise track.

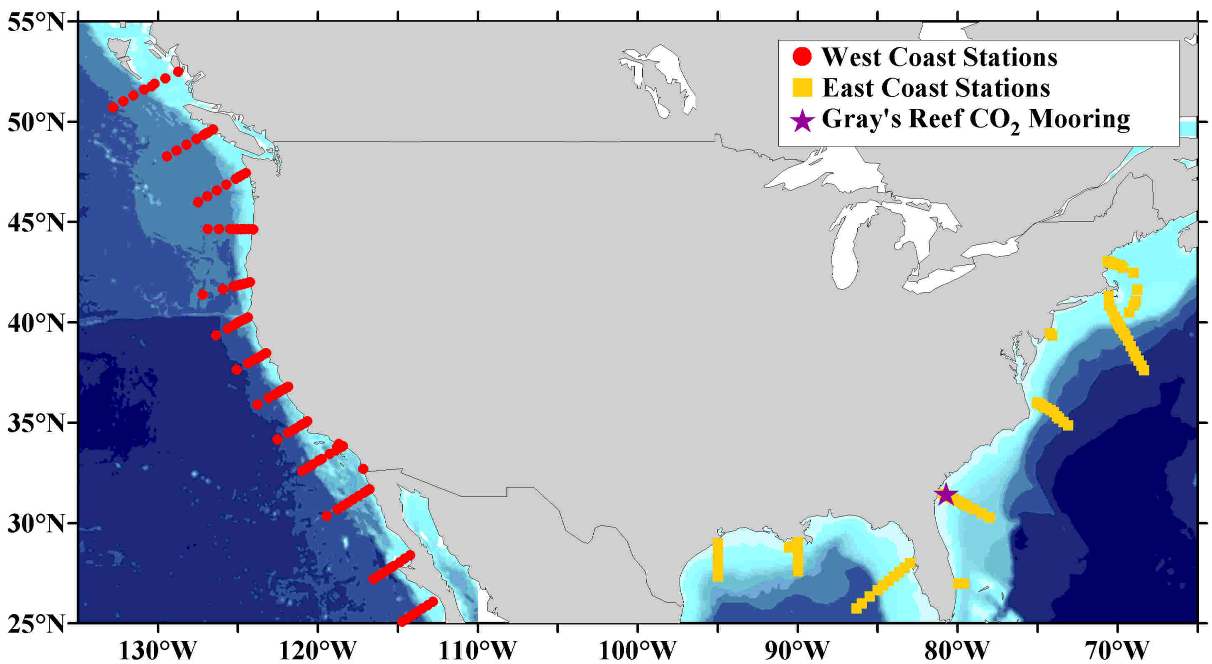

Figure 1. Locations of transects and stations for the NACP West Coast Cruise (red circles) and Gulf of Mexico and East Coast Carbon Cruise (yellow squares) The location of the CO_2 mooring in Gray's Reef National Marine Sanctuary is indicated by a purple star.

During the NACP West Coast Cruise, pCO_2 values at the sea surface ranged between 200 and 800 μatm, indicating that some areas were CO_2 sources and other sinks during the cruise (Figure 2). The lowest pCO_2 values occurred in relatively warm water close to the coast between British Columbia and Oregon, probably reflecting production stimulated by the freshwater input from Puget Sound and the Columbia River plume. Further offshore along the northern part of the cruise track, water temperatures were lower and pCO_2 values indicate that this region was near atmospheric equilibrium, ranging from being a weak source to a weak sink. Along the northern California coastline, the highest pCO_2 values and the lowest sea surface temperatures were observed, indicating that upwelling of CO_2-rich waters was responsible for the highest CO_2 supersaturation observed along the West Coast (Figure 2). The coastal environment south of Monterey, California (~37°N), is spatially heterogeneous, ranging from a localized mild sink off northern Baja to neutral or weak source conditions elsewhere. These results are broadly consistent with observations from July–September 2005 published in the *First State of the Carbon Cycle Report*, showing a strong CO_2 sink off the Pacific Northwest coast, a strong source on the northern California coast, circum-neutral conditions in southern California, and a weak source off of northern Baja California (Chavez et al., 2007). The water upwelling along the northern California coastline and present at 120 m depth throughout the surveyed area is undersaturated with respect to the carbonate biomineral, aragonite (Feely et al., 2008a). Based on results from the 2007 cruise, a proxy algorithm has been developed to calculate aragonite saturation state from hydrographic parameters that have been measured more frequently historically, in this case temperature and oxygen (Figure 3) (Feely et al., 2008b; Juranek et al., accepted). This approach will be useful for hindcasting aragonite saturation states through recent decades. The West Coast Cruise results have made possible the first model-data comparisons, which along with the ability to hindcast saturation states, will help improve the ability of models to accurately forecast coastal carbon cycle and ocean acidification conditions in a high-CO_2 world (Figure 4) (Hauri et al., in press).

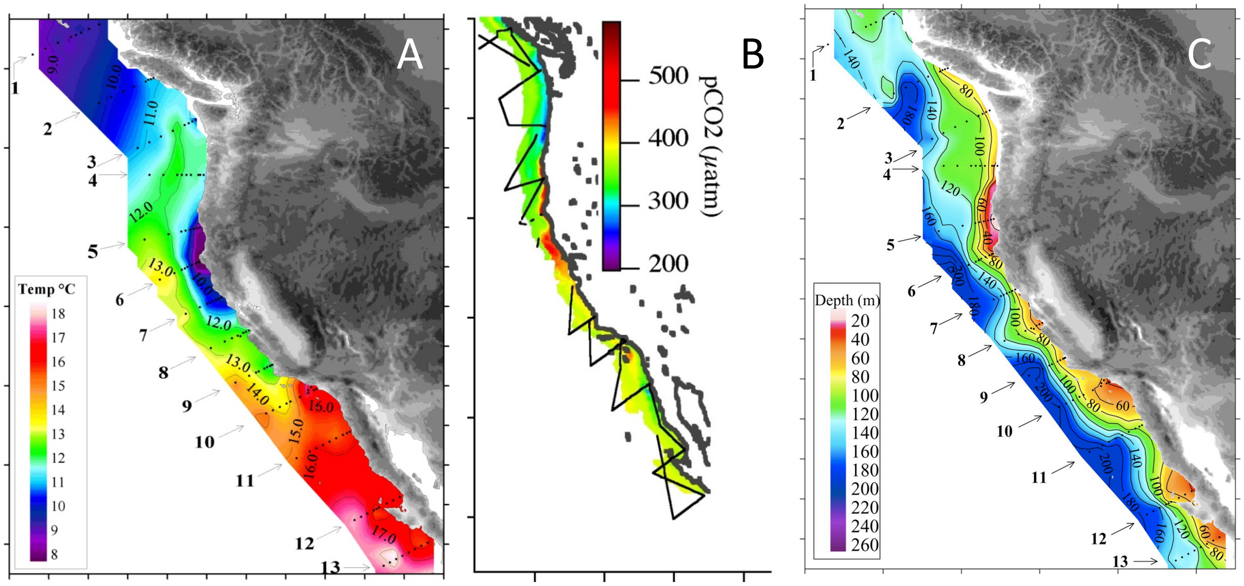

Figure 2. A) Sea surface temperature (SST), B) pCO_2 values, and C) depth to the aragonite saturation horizon measured during the 2007 NACP West Coast Cruise. The trackline of the R/V *Wecoma* is shown by the black lines in B, with sampling lines and stations indicated by numbers and black dots, respectively, in A and C.

From 2006 to 2009, high-resolution atmospheric and surface ocean pCO_2 data were collected by the MAPCO₂ system deployed in Gray's Reef National Marine Sanctuary off Savannah, Georgia. At this site, a strong seasonal cycle in pCO_2 is driven largely by the

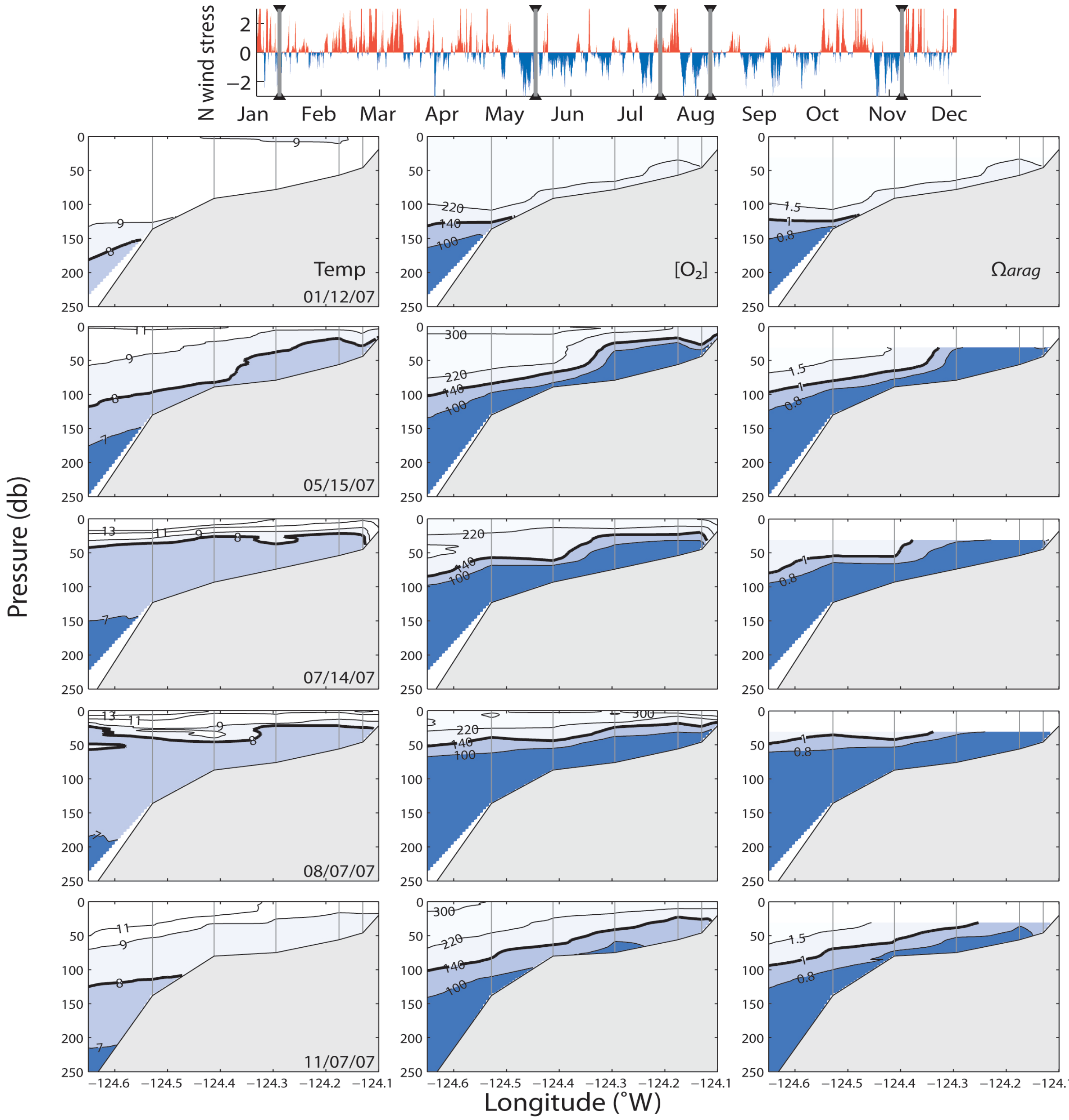

Figure 3: Selected sections of T (°C, left), $[O_2]$ (µmol kg^{-1}, center), and Ω_{arag} (right), for January to November 2007 (Juranek et al., accepted). Ω_{arag} was calculated from T and O_2 data using the regression model developed for depths greater than 30 m by Juranek et al. (accepted). Shown above these is a plot of the northward wind stress (dynes cm^{-2}), with upwelling-favorable winds (southward winds, negative wind stress) in blue and downwelling-favorable winds (northward winds, positive wind stress) in red. Sampling dates for the sections below are indicted by gray bars.

annual temperature cycle, but interesting interannual variation has started to appear in this multi-year record (Figure 5). Observed pCO_2 values indicate that the site acts as a CO_2 sink in the winter when solubility is higher due to lower SST and a source in the summer. Within this record, two distinct blooms appear to have occurred during the spring of 2007. These blooms brought surface pCO_2 well below atmospheric equilibrium values and

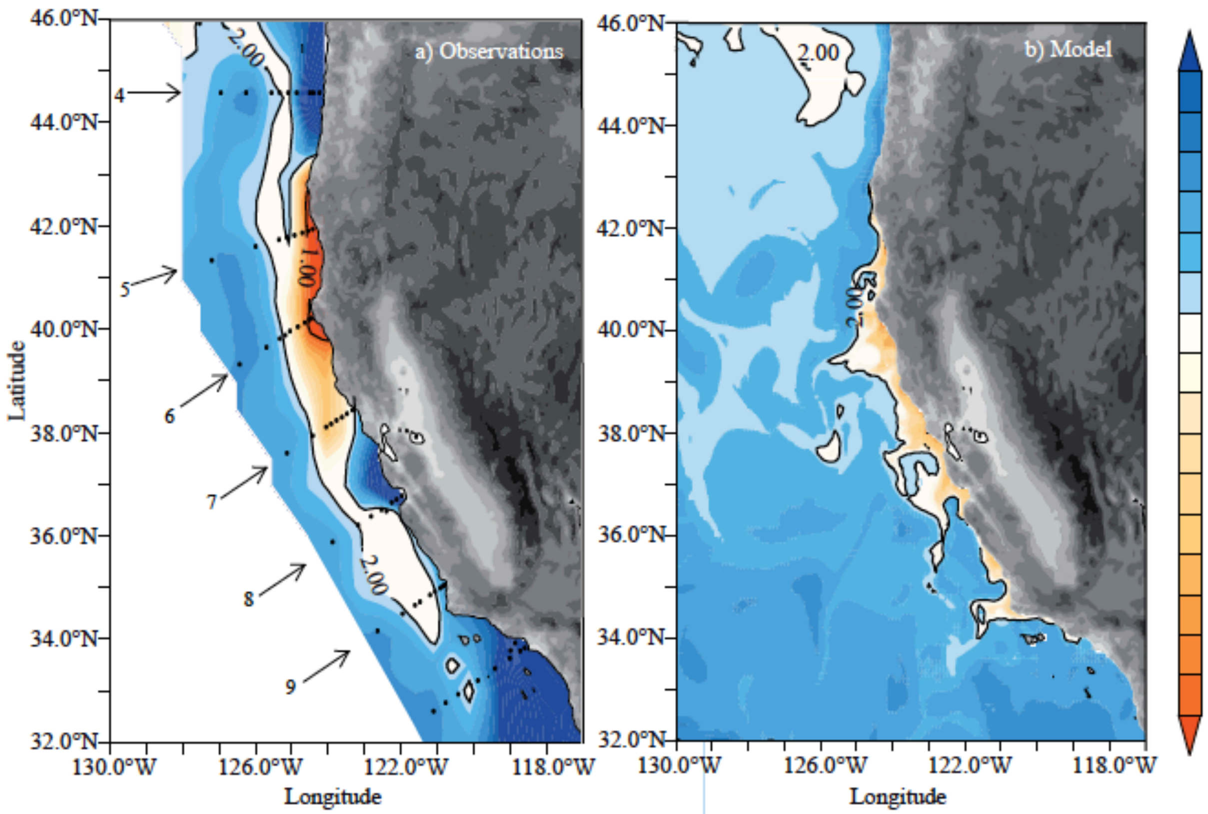

Figure 4. Maps of the surface aragonite saturation state for the California Current System off western North America in mid-May (Hauri et al., 2009 in press). A) Observations are from Feely et al. (2008a) and (B) model results are based on ROMS (Regional Ocean Modeling System) simulations (Gruber et al., 2006).

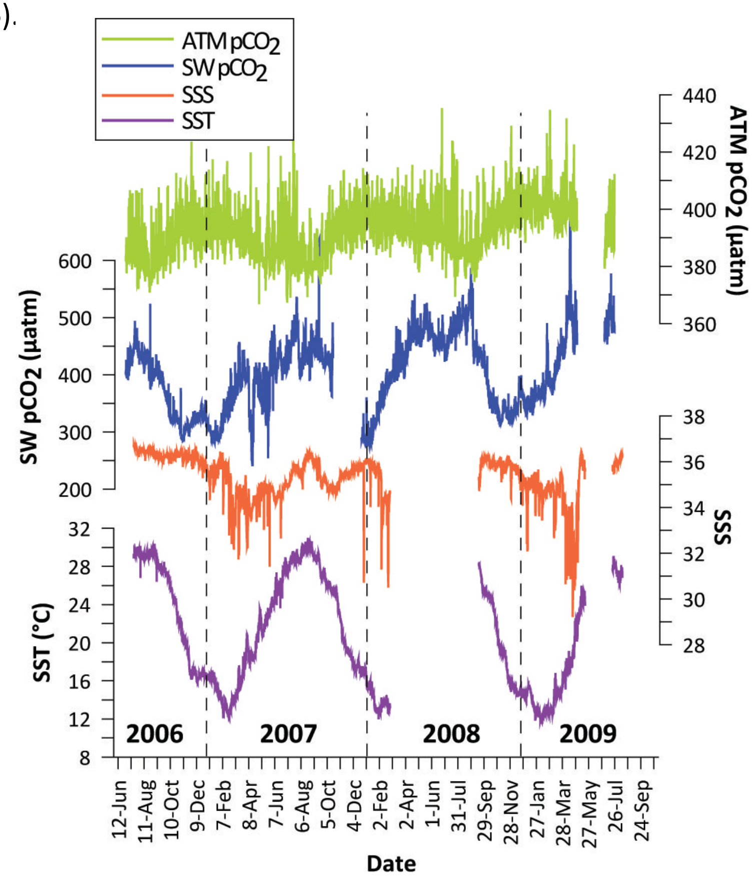

Figure 5. Moored atmospheric (ATM) and surface sea-water (SW) pCO_2, as well as sea surface temperature (SST) and salinity (SSS) observations collected off the Georgia coast from June 2006 to the present (Sabine, Cai, et al., in prep).

coincided with periods of lower SSS, suggesting that the blooms may have been stimulated by river-borne nutrient inputs. Another way to look at interannual variability in this record is to compare the distribution of data across years. For instance, average pCO_2 values were somewhat higher in 2007 (439 ± 27 μatm) than 2006 (403 ± 38 μatm) for the period covered by the system in both years (Jul.-Nov.). The range of sea surface temperatures in 2007, from 12.0 to 31.0°C, was almost identical to 2006, but sea surface salinities varied substantially more in 2007 (30.7–36.5 ppt) than in 2006 (35.3–36.8 ppt). The higher average pCO_2 and more variable salinity values observed in 2007 may reflect the difference in rainfall and river runoff between years. The annual rainfall total in Savannah was 30% below average in 2006 and exactly average in 2007, suggesting that riverine inputs of CO_2, dissolved organic carbon, and fresh water to the South Atlantic Bight would have been higher in 2007.

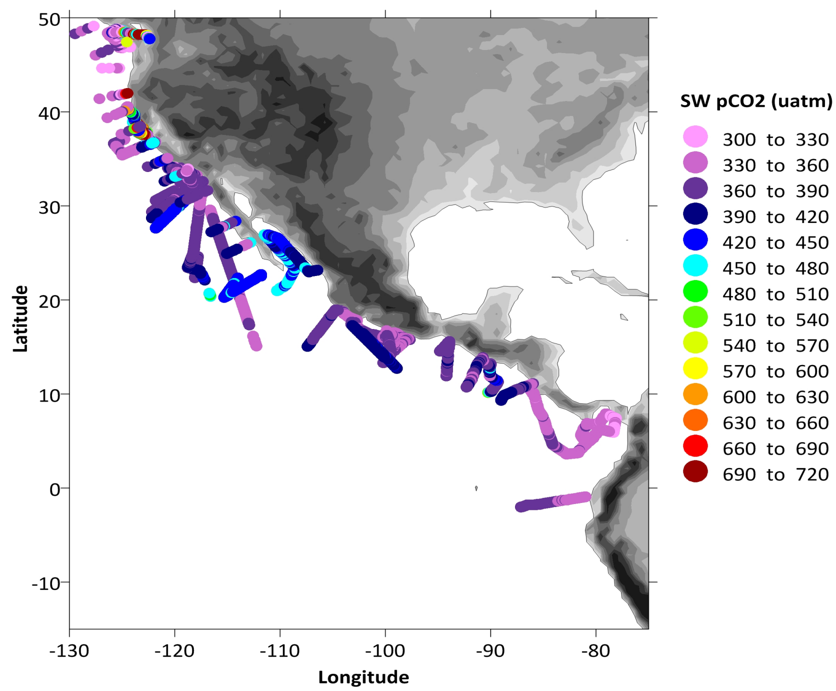

Figure 6. Composite diagram of surface seawater pCO_2 data collected on the Pacific Coast of North America with underway pCO_2 systems on NOAA ships *McArthur II* and *David Starr Jordan* from 2006 to 2008. The ~250,000 new observations were subsampled to keep the figure to a reasonable size (Alin, Feely et al., in prep).

During the period of funding, underway CO_2 systems were installed on NOAA ships *David Starr Jordan* (later replaced by the *Miller Freeman* upon decommissioning) and *McArthur II*. Approximately 300,000 new pCO_2 measurements of near-surface seawater have been collected during NOAA fisheries research cruises with these systems to date (2006–2009) in coastal waters between southern Canada, and Ecuador (~50°N to 5°S, Figure 6). Across this broad area, a large percentage of the observations show the surface water to be undersaturated with pCO_2 with respect to the atmosphere (light purples), due to the high biological productivity in this Eastern Boundary Upwelling System. Supersaturated pCO_2 conditions tend to occur nearest to shore in the strongest upwelling areas and in areas of freshwater influence from British Columbia to central California. Further south, supersaturated conditions can occur further offshore and in the Gulf of California, but the supersaturation is not as pronounced as that seen in the core upwelling areas (Oregon to central California) or the Strait of Juan de Fuca (surface outflow of freshwater between Washington and British Columbia). Observations collected by this project tripled the size of the pCO_2 database relative to the Takahashi database used in the *First State of the Carbon Cycle Report (SOCCR)* North American coastal carbon synthesis (Chavez et al., 2007). The improved seasonal coverage afforded by the ongoing underway CO_2 measurements on coastal research vessels will ultimately allow us to refine estimates of net air-sea CO_2 exchange along the western continental margin, as well as yielding critical insight into inter-annual and long-term variability in the coastal CO_2 system.

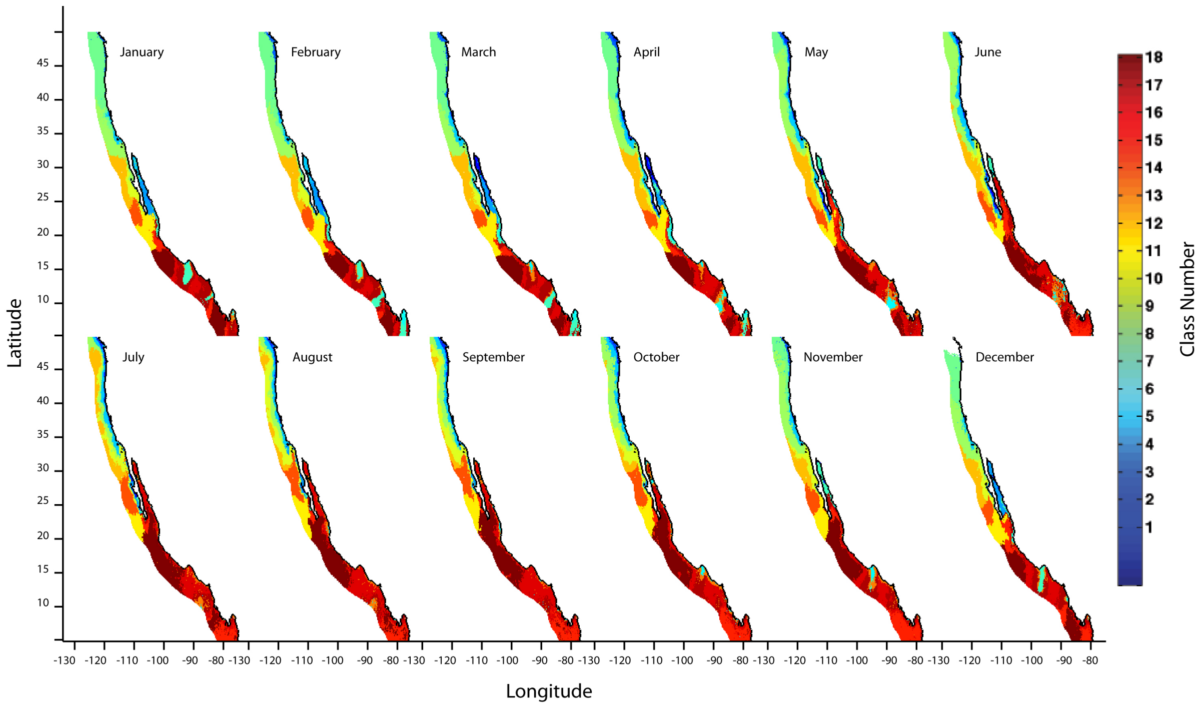

Figure 7. Self-organizing maps for all months of the year. The spatial extent and boundary locations of the 18 biogeochemical regions shift with latitude and the seasonal influence of upwelling-favorable winds in the California Current System and wind jets passing through passes in the Central American cordillera (Hales et al., 2007, 2008, in prep; Alin et al., 2009, in prep).

Advances toward developing mechanistic pCO_2 prediction algorithms to generate monthly pCO_2 and flux maps were greatly facilitated by the influx of new pCO_2 observations in coastal waters along the western margin of North America. The method involves using a neural network approach to generate self-organizing maps based on satellite data related to the environmental controls on sea surface pCO_2 (e.g. temperature, chlorophyll). This approach objectively identifies boundaries among biogeochemical regions by seeking to minimize within-region variability while maximizing among-region variability and defined 18 biogeochemical regions between British Columbia and Panama in an analysis using monthly climatological inputs of SST and chlorophyll (Figure 7). Latitude differentiated three domains: U.S. West Coast, Baja California, and Central America. Cross-shelf distance was also important in the U.S. and Baja, reflecting the role of along-shore wind stress in generating upwelling conditions, but wind jets passing through mountain gaps in Central American played the dominant role in structuring biogeochemical regions there. Surface pCO_2 observations are then assigned to the biogeochemical region in which they were collected and are fit with a mechanistic, non-linear meta-model to predict pCO_2 using remote sensing data. Monthly pCO_2 maps are generated by applying the meta-model to the appropriate remotely sensed data fields and can be transformed into flux maps by using a climatological wind speed data product and a gas transfer parameterization (Figure 8). The outcome of this analysis, using the newly expanded database of coastal surface ocean pCO_2 observations, showed that the western continental margin appears to be a net annual CO_2 sink from 50°N to 5°S, in contrast to the *SOCCR* chapter indicating the northern waters to be a sink and southern waters to be a source.

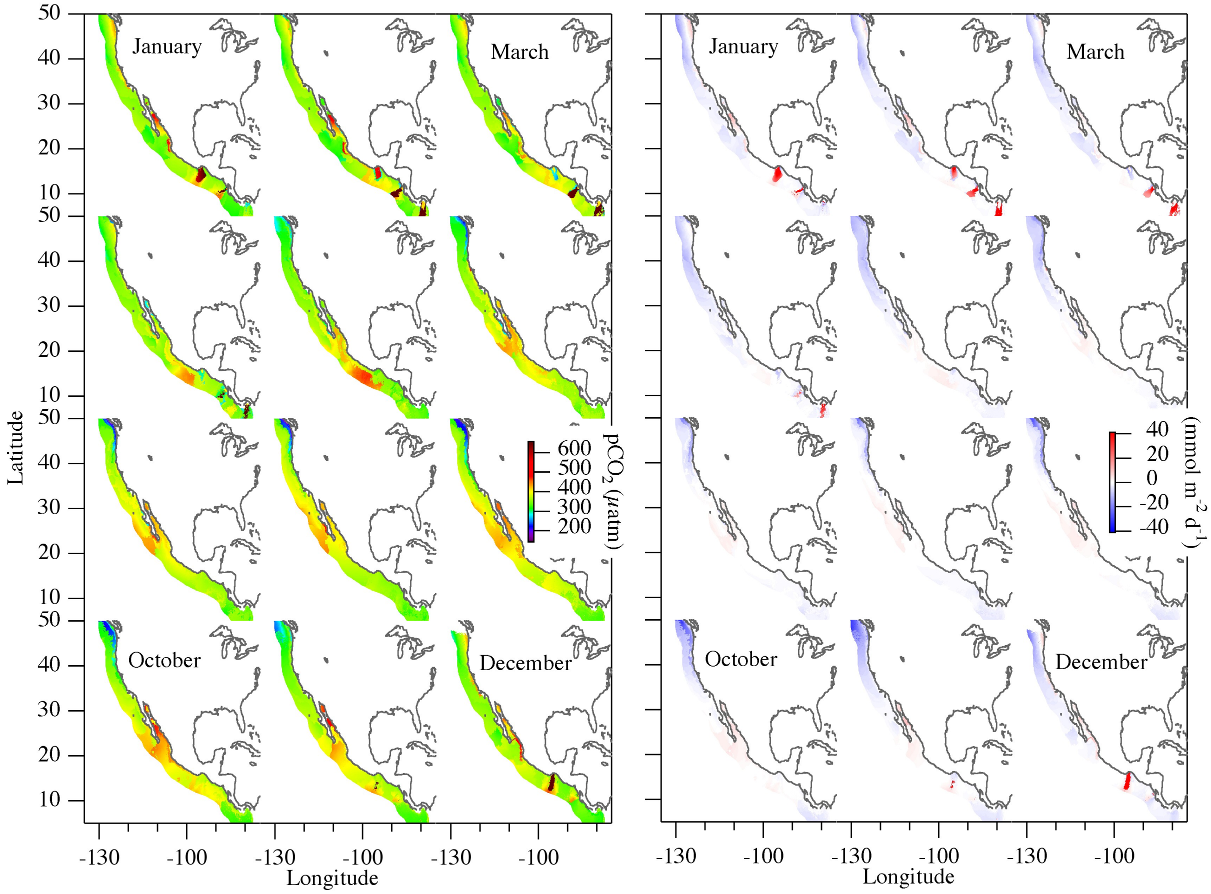

Figure 8. Monthly maps of pCO_2 (left, µatm) and CO_2 flux (mmol m^{-2} d^{-1}) for the western margin of North America (Hales et al., 2007, 2008, in prep; Alin et al., 2009, in prep).

Finally, PMEL developed the Ocean Carbon Data Management System (OCDMS) with a focus on underway data as the primary area for data management work. The LDEO/Takahashi consolidated collection—the largest assembled collection of underway cruise data—was the main target of these efforts. In addition, we applied these tools to individual cruise data from PMEL and AOML. The work involved developing a new database schema; tools and procedures for ingesting the data; quality control filters; tools and techniques for high-speed retrieval of selected subsets from the collection; and an LAS-based system (user interface and products) for visualization of the data and interaction with it (Figures 9 & 10). The process of ingesting data as a collection into a database provided a final filter on several aspects of quality control, including flagging out-of-range data and duplicates. When applied to the LDEO collection (>3.2 million records, including open ocean carbon observations), the filters developed for the OCDMS identified 1.1% of data as out-of-range (not plausible) and 0.4% as duplicates, which can cause weighting errors during data analysis. In this way, the OCDMS utility contributed to imposing stringent data quality standards for community CO_2 databases such as the LDEO collection.

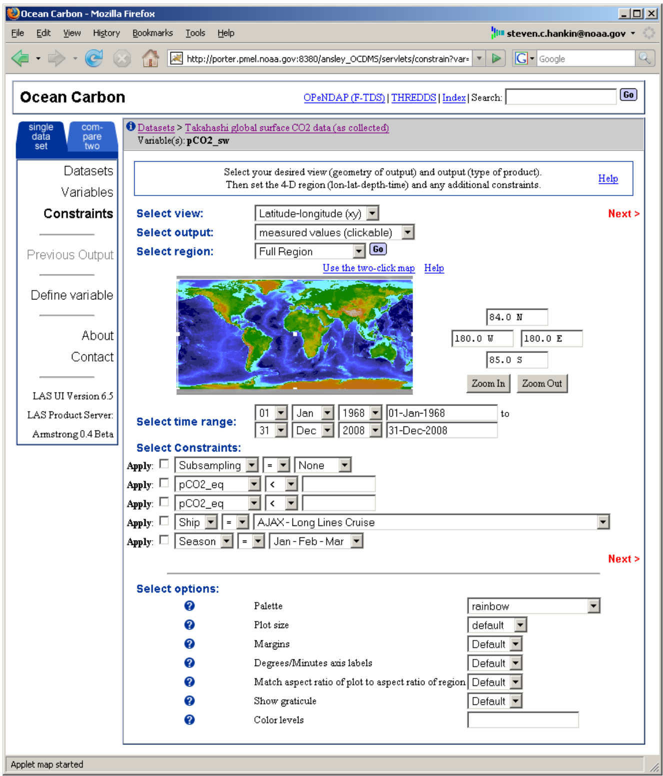

Figure 9 (left). A snapshot of the OCDMS User Interface.

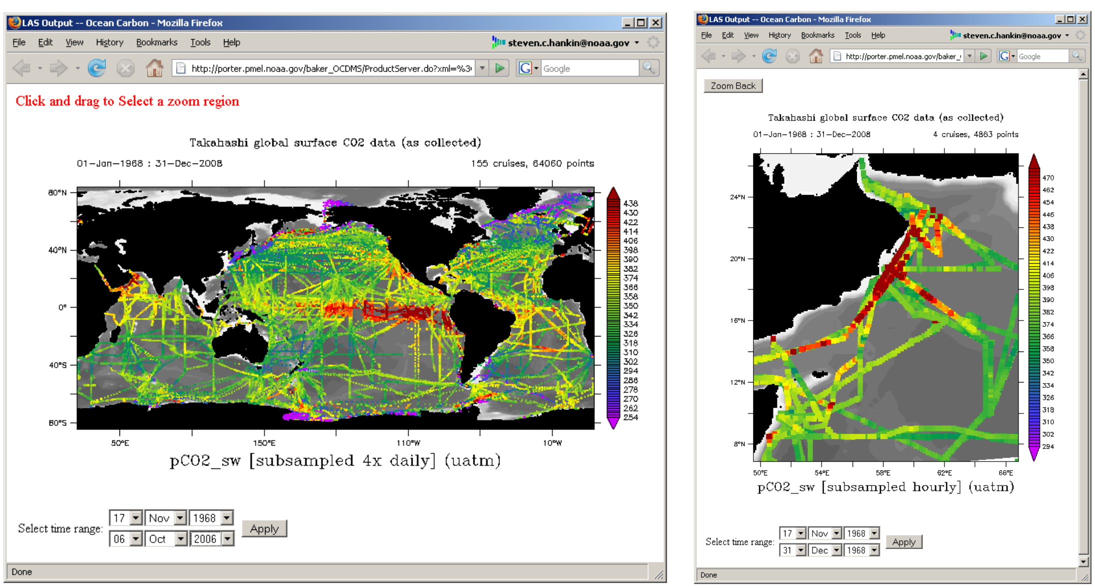

Figure 10 (below). The entire (1968-present) LDEO global seawater pCO_2 database as shown in OCDMS (left) and a zoomed image of a coastal region (right).

During 2008, OCDMS version 2.0 was complete, installed, and made operational at CDIAC and PMEL. This data server provides 1) a "cruise map" visualization that provides the investigator with flexibility and control over searches; 2) a "sortable table" product that enhances the user's ability to access subsets of the database by cruise, PI, ship, or other metadata; 3) up to date versions of the LDEO (Takahashi) and CARBOOCEAN/IOCCP data collections (from Benjamin Pfeil and Are Olsen at Bjerknes Centre for Climate Research); and 5) prototypes of gridded carbon fields, based upon regressions of satellite data against underway cruise measurements that were developed by Chris Sabine as part of an effort to define "metrics" for the ocean carbon sampling program.

4.0 East and Gulf Coast Results and Accomplishments (Wanninkhof, Peng, Zhang, Langdon, Cai)

A major accomplishment of the East and Gulf coast team was the successful completion in 2007 of the first North American Carbon Program (NACP) Gulf of Mexico and East Coast Carbon Cruise (GOMECC), led by Chief Scientists Tsung-Hung Peng and Chris Langdon. The 26-day cruise on the R/V *Ronald H. Brown* left Galveston, Texas, on July 10 and arrived in Boston, Massachusetts, on August 4, 2007. The thirty participating scientists were supported by these efforts and several other funding sources. A total of 90 CTD/O_2 stations were occupied along nine transects orthogonal to the coast during the cruise between Galveston and the Gulf of Maine (Figure 1). Water samples collected with a 24-bottle rosette at each CTD station were analyzed for salinity, oxygen, nutrients, dissolved inorganic carbon, total alkalinity, pCO_2, dissolved organic matter, colored dissolved organic matter, particulate organic carbon, carbon monoxide, halocarbons, alkyl nitrates, and phytoplankton pigments. In addition, underway systems measured near-surface seawater and atmospheric pCO_2, DIC, pH, ammonium, carbon monoxide, halocarbons, and bio-optical properties. A spectrophotometric pH profiler was also deployed on the CTD to measure pH profiles at stations shallower than 1000 m. The underway pCO_2 systems measured both near-surface and atmospheric pCO_2 values using two different systems to provide side-by-side comparisons with a new system built by General Oceanics. The data are served from http://www.aoml.noaa.gov/ocd/gcc/GOMECC/. Surface water pCO_2 values were supersaturated almost everywhere along the cruise track, with the exception of near large river mouths in the northern Gulf of Mexico (Figure 11). The pCO_2 data sets show that broad regions of the Gulf of Mexico and eastern coastline appeared to be CO_2 sources at the time of the cruise.

Oxygen saturation was measured by an optode placed in the ship's seawater line and calibrated against discrete oxygen samples determined by Winkler titration (Figure 11). Oxygen supersaturation, as well as elevated chlorophyll levels (not shown), at the stations closest to the coast reflected high rates of primary production, likely fueled by river-borne nutrients. Exceptionally high oxygen saturation levels (115–125%) were observed in the Gulf of Maine and to the southeast of Cape Cod. On average oxygen was supersaturated at 105% along the cruise track. This indicates that net community production in the mixed layer was positive over approximately the week prior to sampling across a broad swath of the Gulf of Mexico and East Coast and that the phytoplankton were taking up CO_2 from the water. Taken together the picture that emerges is that the region is transitioning from being a strong source of CO_2 to a weaker source as phytoplankton take up CO_2. Time-series observations such as those performed on the SAB will reveal whether this transition is significant or only short-lived (e.g. Jiang et al., 2008).

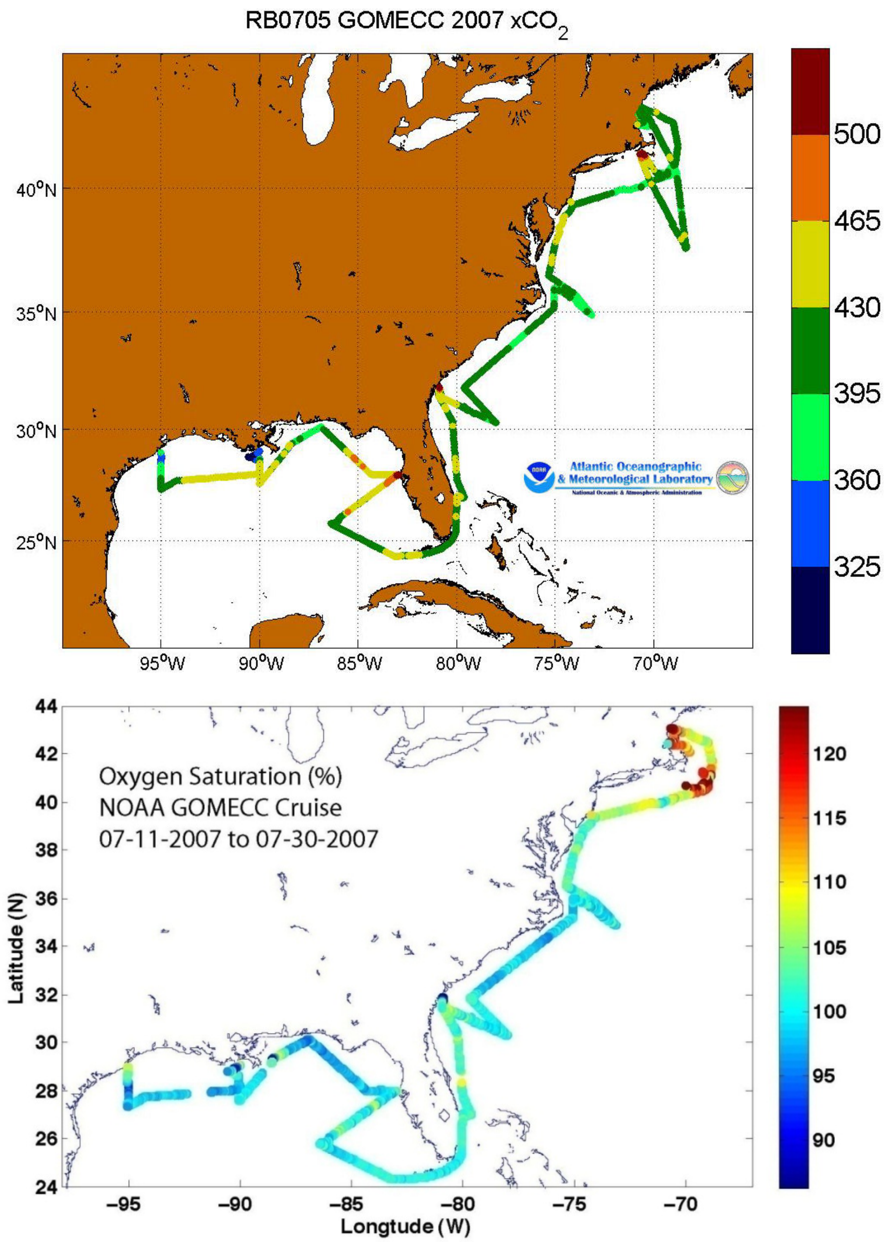

Figure 11. Surface seawater A) CO_2 and B) O_2 observations collected by the underway pCO_2 and O_2 systems on GOMECC.

Atmospheric pCO_2 values were quite variable, ranging from 365 to 415 µatm, illustrating the influence of changing wind direction on the atmospheric source observed (Figure 12). Near the coast the marine air values are influenced by sources and sinks of CO_2 on land. The low atmospheric pCO_2 values along the SE coast reflect the active CO_2 uptake by terrestrial ecosystems during the summer. In coastal regions, delta pCO_2 values ($\Delta pCO_2 = pCO_2sw - pCO_2air$) are affected not only by surface water pCO_2 but also by the highly variable atmospheric pCO_2, so variations in air CO_2 concentrations have a direct effect on air-sea CO_2 fluxes (Figure 13).

Air-sea CO_2 fluxes for the period of the GOMECC cruise were estimated using the ΔpCO_2 data and 5-day averaged, remotely sensed winds (QuikSCAT) and SST fields (AVHRR) provided by NOAA Coast Watch at 0.5° resolution. Overall, the coastal region was a strong source of CO_2 during the cruise, interrupted by localized sink regions directly associated with continental run-off (Figure 13). Along the Gulf of Mexico coastline, a strong positive

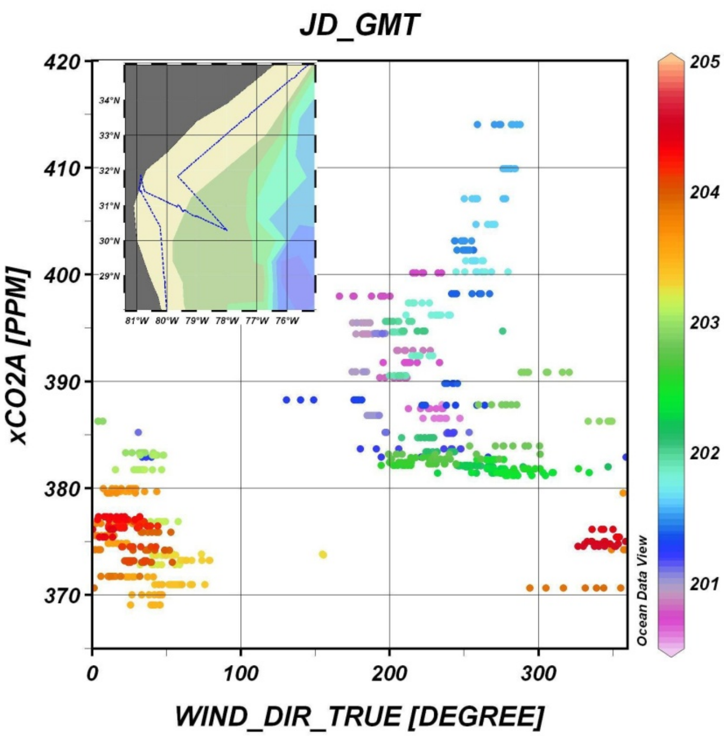

Figure 12. Air CO_2 concentrations for the transect along the SE US coast show low values when the winds come from land (0–90°) reflecting terrestrial photosynthesis.

correlation between ΔpCO_2 and salinity confirms that riverine outflows produce strong CO_2 sink zones. In contrast, along the Southeast coast, the negative correlation between ΔpCO_2 and salinity reflects different TA and DIC end-members for the continental run-off in the region, such as the strong inputs of CO_2 and DOC in low alkalinity waters from marshes along the Southeast coast. Along the Northeast coast, the sources are somewhat smaller than further offshore (offshore data are from Explorer of the Seas runs), which we attribute to higher biological productivity near-shore (supported by the high oxygen supersaturation described above). Air-sea CO_2 flux estimates within the coastal region were calculated for 10-day stretches of the cruise representing the three major regions covered: northern Gulf of Mexico (2.03 ± 2.03 mmol m^{-2} d^{-1}), Southeast coast (3.26 ± 2.22 mmol m^{-2} d^{-1}), and Northeast coast (1.26 ± 1.07 mmol m^{-2} d^{-1}).

New underway measurements of ammonium in the surface water were carried out during the GOMECC cruise. Ammonium concentrations were measured by a shipboard flow-injection analyzer with fluorescence detection. The highest ammonium concentrations were found at stations near the coastline, apparently derived from terrestrial sources (Figure 14). Surface ammonium concentrations decrease rapidly from the coast to the open ocean. Typical ammonium concentrations in shelf surface waters are in the range of 0.05 to 0.15 µM, whereas observed coastal values frequently fell between 0.21 and 0.56 µM.

Discrete measurements performed on GOMECC also yielded high quality data. Parameters of particular interest to this project include TA, DIC, discrete pCO_2, dissolved oxygen, nutrients, and spectrophotometric pH (provided by R. Byrne, USF). Good agreement was seen between measured and calculated CO_2 system parameters collected by both underway and discrete methods. Figure 15 shows sections of several critical geochemical parameters on the Mississippi River transect from GOMECC. A unique feature of the Gulf of Mexico is that TA is higher in surface water and lower at depth, while DIC is higher in deep water. Minimum pH and maximum pCO_2 values were observed around 600-m depth, in the middle of the broad dissolved oxygen minimum between 400 and 700 m. Dissolved oxygen was also depleted in bottom waters on the continental shelf. Aragonite saturation states,

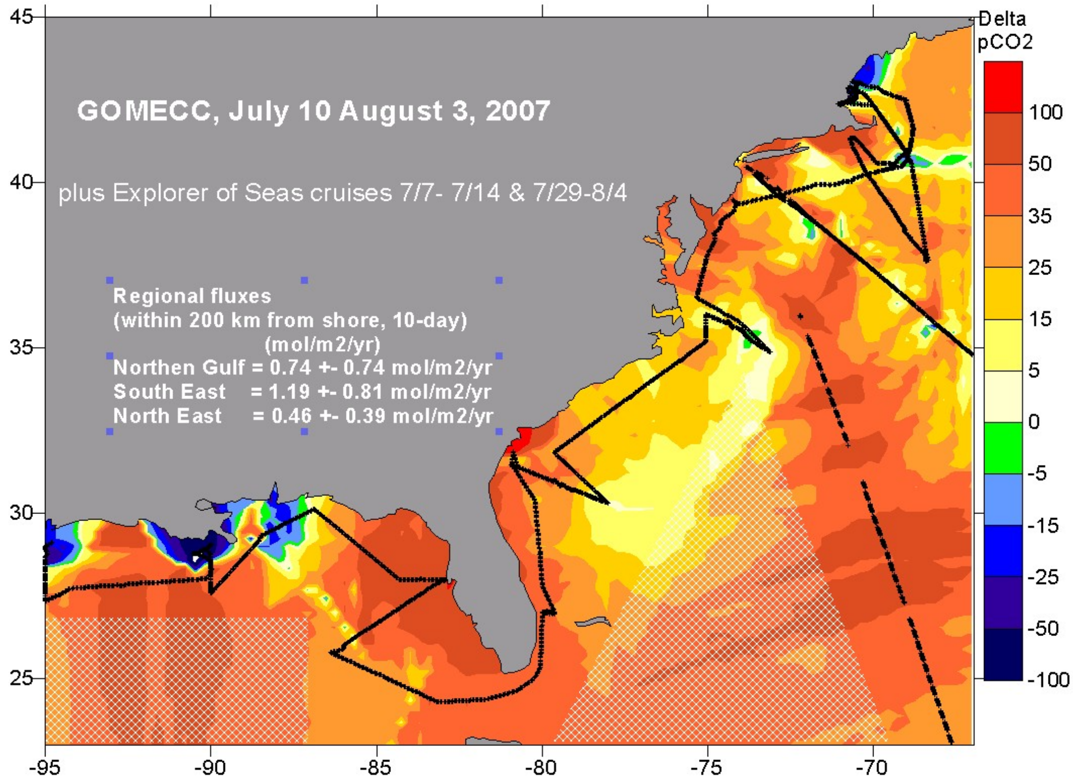

Figure 13. Delta pCO_2 values measured during GOMECC and by the *Explorer of the Seas* underway system during the same period of time.

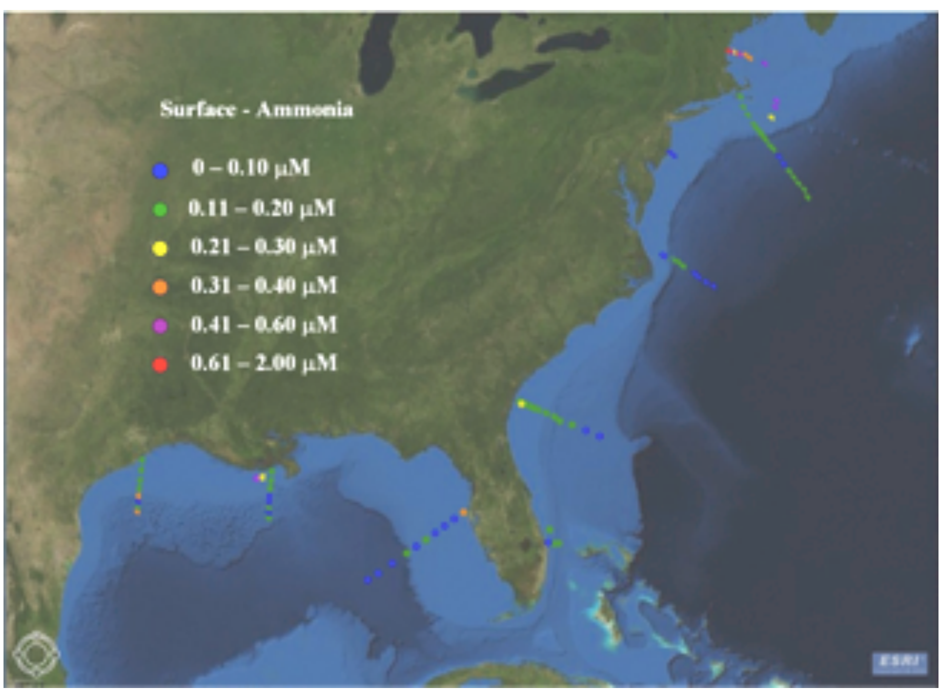

Figure 14. Surface ammonia concentrations observed on GOMECC.

calculated from TA and DIC, indicate that the bottom waters of the northern GOM (outer shelf and slope) are only slightly above saturation. To what extent this observation is the result of anthropogenic ocean acidification is under investigation. However, it is clear that further ocean acidification would easily push the bottom water toward undersaturation.

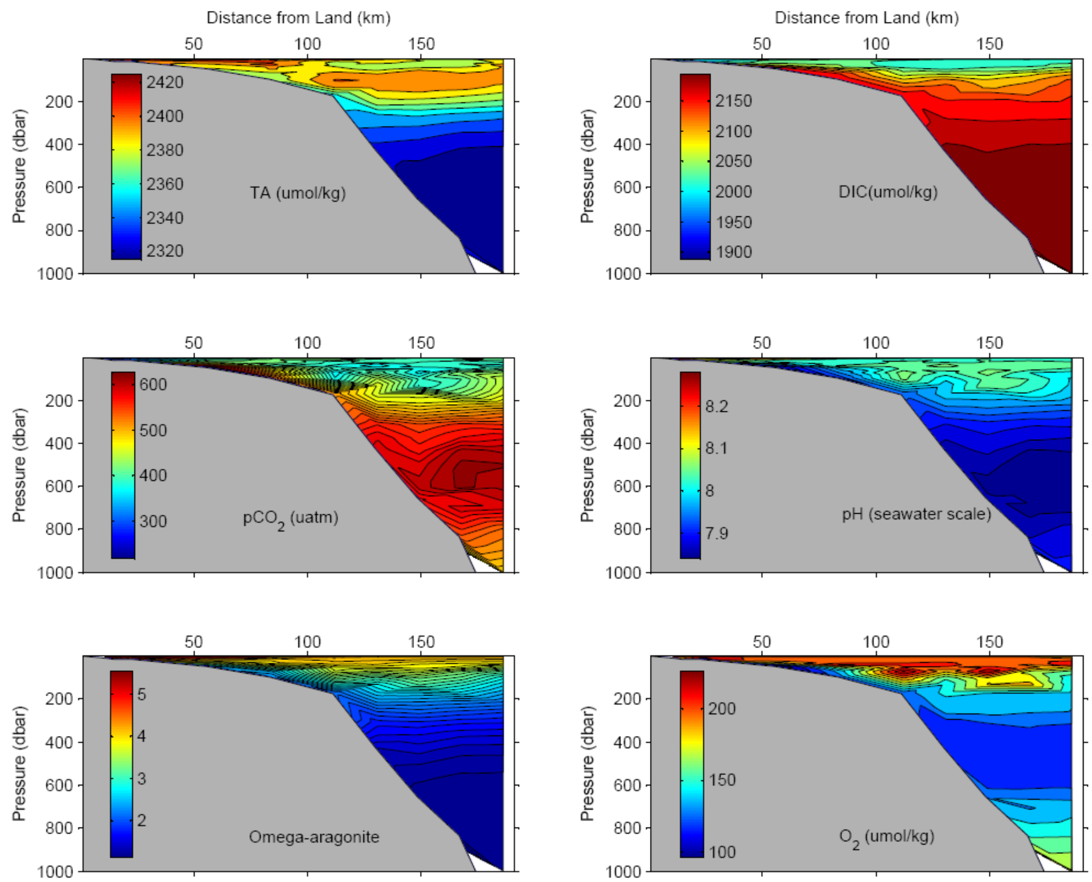

Figure 15. Sections of alkalinity (TA), dissolved inorganic carbon (DIC), pCO_2, pH, aragonite saturation state (omega-aragonite), and dissolved oxygen on the Mississippi River transect, one of the three transects in the Gulf of Mexico during GOMECC (Cai et al., in prep.).

In addition to work related to GOMECC, progress was also made with data synthesis for carbon cycling observations in the South Atlantic Bight (SAB). Partial pressures of carbon dioxide in surface seawater were measured during six cruises on the SAB from January 2005 to May 2006 (Figure 16). These high-resolution pCO_2 data allowed us to create the first maps of observed sea surface *p*CO_2 over the SAB for all seasons. Contrary to an earlier study with limited spatial and seasonal coverage, this study showed that the SAB is a net sink of atmospheric CO_2 on an annual basis (-0.78 ± 0.50 mol m^{-2} yr^{-1}). The inner shelf is a source of +0.77 mol m^{-2} yr^{-1}, while the middle and outer shelves are sinks of -1.46 and -1.63 mol m^{-2} yr^{-1}, respectively. Seasonally, the SAB shifts from a sink of atmospheric CO_2 in winter to a source in summer, as also observed at the Gray's Reef CO_2 mooring. The annual cycle of SST plays a dominant role in controlling the seasonal variation of pCO_2. The inverse correlation across seasons between wind speeds and ΔpCO_2 values is an important factor in determining the net annual air-sea CO_2 exchange.

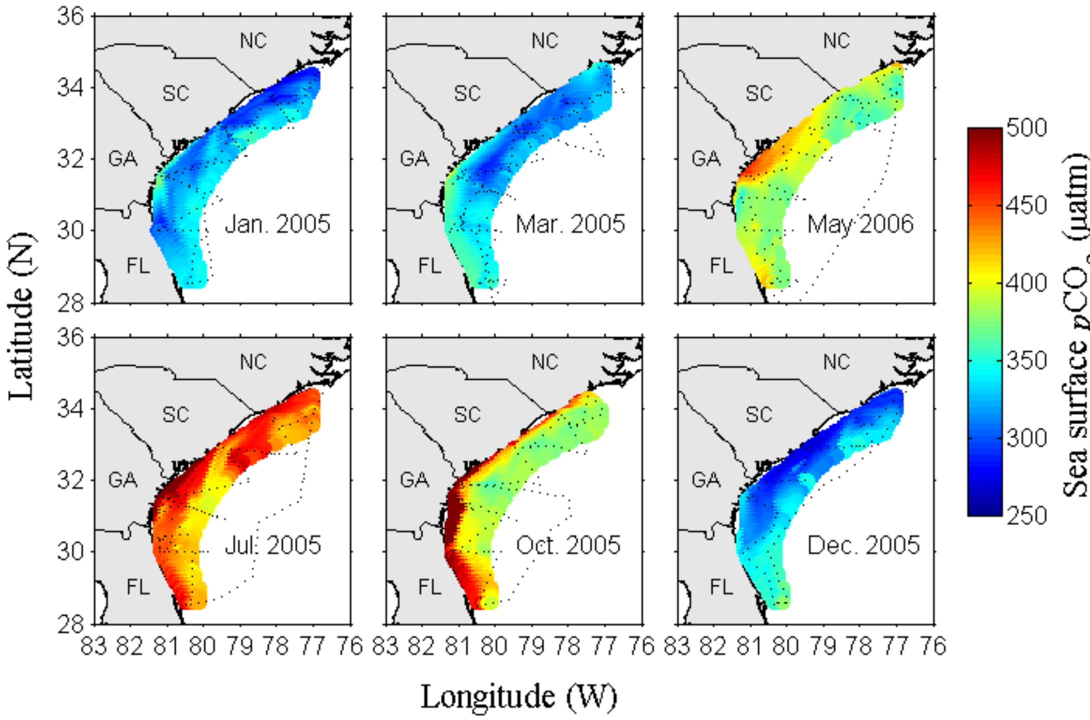

Figure 14. Maps of observed sea surface pCO_2 on the U.S. South Atlantic Bight for all sampled months (Jiang et al. 2008). The colored contours are from triangle-based linear interpolation. Dotted lines show the ship track.

During the period of funding, several ships were instrumented with underway pCO_2 systems either for individual cruises or on a longer-term basis. Surface pCO_2 observing ships serving the East Coast included the NOAA ship *Ronald H. Brown*, R/V *Walton Smith*, cruise ship *Explorer of the Seas*, and container ship *Reykjafoss*, and those in the Gulf of Mexico included NOAA ship *Gordon Gunter* and methanol tanker *Las Cuevas*. In addition, an EPA-led effort on the EPA ocean survey vessel *Bold* resulted in seasonal coverage of CO_2 distributions in the Mississippi River plume in the northern Gulf of Mexico. The coastal underway pCO_2 observing effort by these investigators and outside collaborators was strongly leveraged by other sources of funding and has contributed >200,000 new pCO_2 observations on the Gulf and East coasts (Figure 17). The new observations are facilitating critical advances in our understanding of the annual air-sea CO_2 exchange in the Gulf of Mexico relative to the synthesis in the *SOCCR* coastal oceans synthesis, which was extremely data-limited but suggested that the Gulf coastal oceans were a strong annual source of CO_2 in the context of North American coastal ocean fluxes (Chavez et al., 2007). A more recent synthesis using the new data and an algorithm developed to extrapolate observations based on relationships between pCO_2, SST, and SSS suggests instead that the northern Gulf of Mexico is a net annual sink for CO_2 rather than a strong source (Figure 18)

(Wanninkhof et al., 2009).

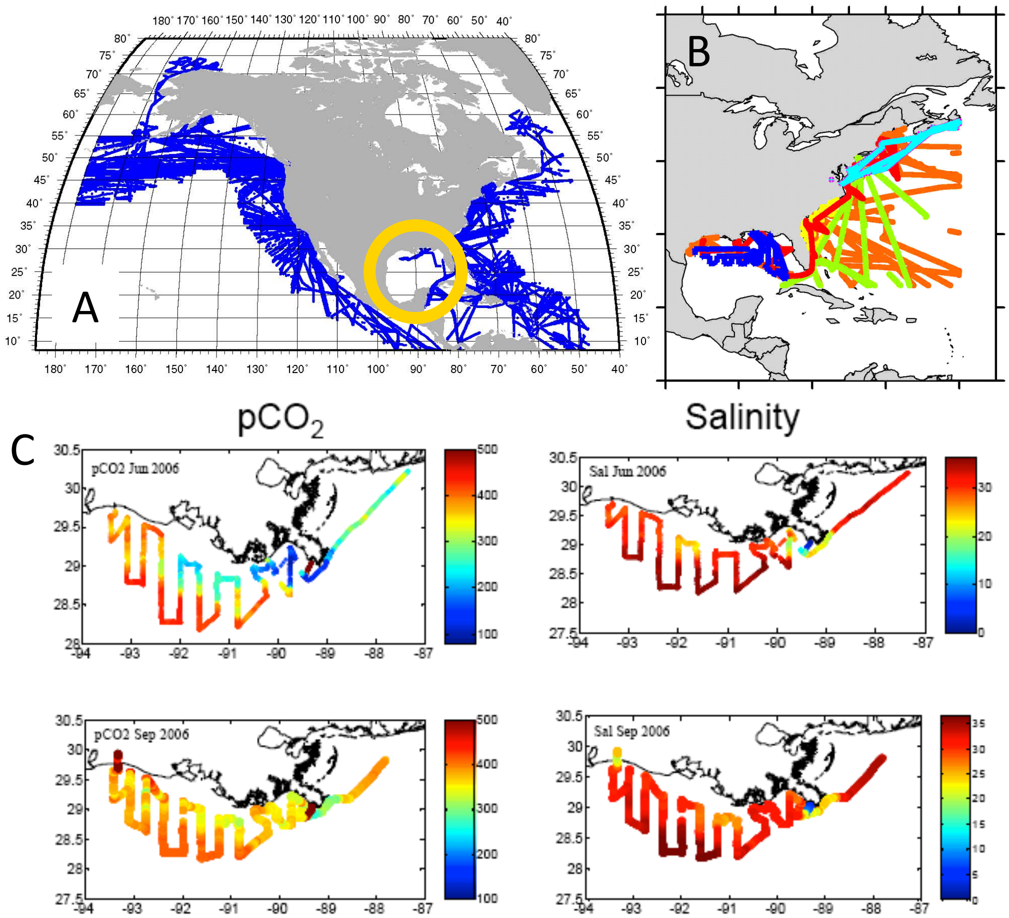

Figure 17. A) Sampling map from *SOCCR* coastal CO_2 synthesis showing sampling deficit in the Gulf of Mexico (Chavez et al., 2007). B) Tracklines of new CO_2 observations made on East and Gulf coasts by AOML team 2006−2008. C) Some of the seasonal pCO_2 and salinity observations made in the area of Mississippi River plume influence in the northern Gulf of Mexico in 2006 by Cai and colleagues.

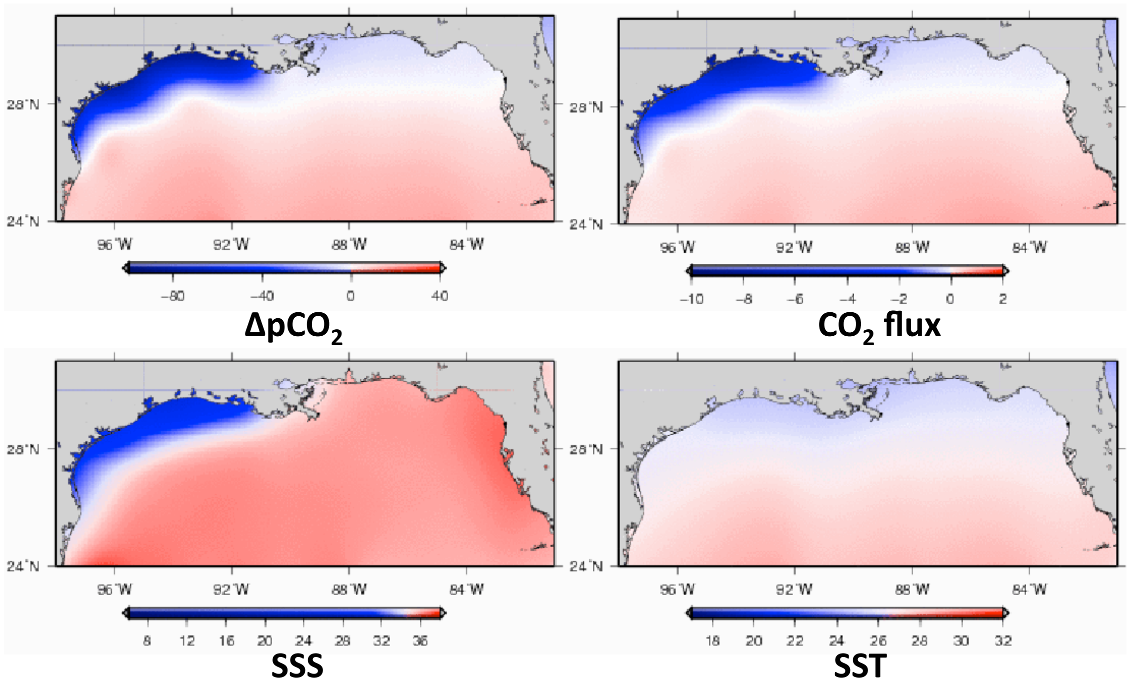

Figure 18. Example of monthly flux map products for the northern Gulf of Mexico for October 2008 (Wanninkhof et al., 2009). The top left panel is the ΔpCO_2 with blue indicating a negative value (a sink) and red a positive value (source). The top right panel is the flux with blue shading indicating a flux into the ocean and red a flux out of the ocean. The bottom left panel is the SSS derived from the RTOFS model with blue shading indicating areas where S<34.5. The algorithm with SSS and SST is applied to the data in these pixels. The bottom right panel is SST from the IO product with a transition in color scale from blue to red at 26.3 which is the temperature where the ΔpCO_2 changes from negative to positive.

5.0 Summary of Major Results

Several important advances in our understanding of carbon cycling along North American continental margins were made possible by the increased coastal CO_2 observational network that this grant largely funded. Large-scale hydrographic cruises on all coasts provided insights into the relative susceptibility to ocean acidification impacts of coastal ecosystems. On the West Coast, upwelling plays a key role in bringing subsurface water masses depleted in oxygen and rich in nutrients and CO_2, with low pH and aragonite saturation states onto the continental shelf from Canada to Mexico and to the surface in more localized areas like northern California (Feely et al., 2008a). On the East Coast, work by our collaborators has demonstrated the role of riverine inputs to coastal oceans in exacerbating acidification conditions (Salisbury et al., 2008), and observations from the GOMECC cruise suggest that this is also an important consideration for the Gulf of Mexico, another river-dominated coastline (Cai et al., in prep.). Finally, the existence of these large-scale hydrographic datasets is facilitating the development of novel algorithms to hindcast (and ultimately forecast) acidification conditions based on more widely measured parameters such as oxygen, temperature, and salinity (Feely et al., 2008b; Juranek et al., accepted).

Table 1. Air-sea exchange flux estimates for North American continental margins made using various methods.

Coastal area (method[a])	Latitude (N)	Short-term CO_2 flux rates[b] (mmol m^{-2} d^{-1})	Annual CO_2 flux rate (mol m^{-2} y^{-1})	Total CO_2 flux (Tg C y^{-1})	Source
North America					
All (clim.)	~8–75°	n.a.	n.a.	2 ± 36[c]	Chavez et al. (2007)
Pacific Coast					
SE Alaska–Panama (clim.)	~8–55°	n.a.	n.a.	−13 ± 26[c]	Chavez et al. (2007)
U.S. West Coast–Baja (SOM)	22–50°	−20 to +20	n.a.	−17	Hales et al. (2007)
Mexico–Panama (SOM)	5–25°	n.a.	n.a.	−0.5	Hales et al. (2008)
U.S. West Coast (ROMS)	24–48°	n.a.	n.a.	weak source	Plattner et al. (2008)
U.S. Central America (SOM)	5–50°	n.a.	n.a.	−30	Alin et al. (2009)
Gulf of Mexico Coast					
All plus Caribbean (clim.)	8–32°	n.a.	n.a.	+38 ± 14[c]	Chavez et al. (2007)
Mississippi River plume		n.a.	n.a.	−0.34	Cai in Robbins et al. (2009)
Northern Gulf	24–32°	n.a.	n.a.	−12	Wanninkhof et al. (2009)
Northern Gulf	~8–32°	2.03 ± 2.03	n.a.		GOMECC
Atlantic Coast					
New England–Caribbean (clim.)	~8–45°	n.a.	n.a.	−8 ± 16[c]	Chavez et al. (2007)
Northeast	~35–40°	1.26 ± 1.07	−0.43 to −0.84	n.a.	GOMECC, Boehme et al. (1998)
Southeast	28–35°	3.26 ± 2.22	−0.78 ± 0.50	n.a.	GOMECC, Jiang et al. (2008)

[a] Methods are abbreviated as follows: clim. = climatology, SOM = self-organizing maps, ROMS = regional ocean modeling system.

[b] Short-term fluxes are fluxes on weekly to monthly timescales calculated on the basis of observations made on the 2007 West Coast and GOMECC cruises.

[c] The Chavez et al. (2007) fluxes cited in this table differ somewhat from those cited in the text of this report. The numbers cited in the text are those for the first 1° box offshore. The numbers cited in this table are for the coastal zone up to ~4° offshore, which is closer to the areas used in the syntheses by Hales, Plattner, Alin, and co-authors.

Along the Atlantic, Gulf, and Pacific coastlines of North America south of the Canadian border, the increase in spatial and temporal sampling coverage by moored and underway surface pCO_2 systems facilitated the next generation of coastal air-sea CO_2 syntheses, which was the overarching goal of this proposal (Jiang et al., 2008; Wanninkhof et al., 2009; Hales et al., 2007, 2008; Alin et al. 2009). These syntheses have shown that coastal air-sea CO_2 flux estimates in the *First State of the Carbon Cycle Report* (Chavez et al., 2007) were not necessarily of the correct sign (Table 1). *While these advances have been important, it is clear that much work remains to improve our understanding of uncertainties, inter-annual variability, directional trends, and the key factors driving these patterns in coastal air-sea exchange*. Despite the gaps in our knowledge, the skeleton of a coastal carbon observatory established in U.S./North American waters has provided a model for the development of a community vision for a global coastal carbon observation system (Borges et al., accepted).

6.0 Publications

Papers:

Amornthammarong, N. and **J.-Z. Zhang** (2008) Shipboard Fluorometric Flow Analyzer for High-Resolution Underway Measurement of Ammonium in Seawater. *Analytical Chemistry*, 80(4): 1019-1026; (Article) DOI: 10.1021/ac701942f

Borges, A.V., **S.R. Alin**, F.P. Chavez, P. Vlahos, K.S. Johnson, J.T. Holt, and 43 others (including **W.J. Cai**, **R.A. Feely**, **B. Hales**, and **R. Wanninkhof**) (accepted). A global sea surface carbon observing system: inorganic and organic carbon dynamics in coastal oceans. Community White Paper for *OceanObs '09*.

Cai, W.-J., X. Hu, W.-J. Huang, Y. Wang, **T.-H. Peng**, and X. Zhang (2009), Alkalinity distribution in the Western North Atlantic Ocean margins, *J Geophys. Res.-Oceans*, revised and under 2nd review.

Cai, W.-J. and Lohrenz, S. 2009. Carbon, nitrogen, and phosphorus fluxes from the Mississippi River and the transformation and fate of biological elements in the river plume and the adjacent margin. In: K.-K. Liu, L. Atkinson, R. Quiñones and L. Talaue-McManus (eds). *Carbon and Nutrient Fluxes in Continental Margins: A Global Synthesis*. Springer-Verlag, New York.

Chavez, F., T. Takahashi, **W.-J. Cai**, G.E. Friederich, **B.E. Hales**, **R. Wanninkhof**, and **R.A. Feely** (2007). Chapter 15. The Coastal Ocean, in The First State of the Carbon Cycle Report (SOCCR): The North American Carbon Budget and Implications for the Global Carbon Cycle , edited by A. W. King and L. Dilling, U.S. Climate Change Science Program Synthesis and Assessment Product 2.2, Washington DC.

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Guo, X., **Cai, W-J.**, Huang, W-J., Wang, Y., Chen, F., Murrell, M.C., Lohrenz, S. Dai, M., Jiang, L-Q. and Culp, R. 2009. CO_2 dynamics and community metabolism in the Mississippi River plume. Submitted to *Limnol. & Oceanogr*.

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Hauri, C., N. Gruber, G.-K. Plattner, **S. Alin, R.A. Feely, B. Hales**, and P.A. Wheeler (2009, in press). Ocean acidification in the California Current System. *Oceanography*.

Huang, X.-L., and **J.-Z. Zhang** (2008) Kinetic Spectrophotometric Determination of Submicromolar Orthophosphate by Molybdate Reduction. *Microchemical Journal*, doi:10.1016/j.microc.20007.12.001.

Jiang, L.-Q., **W.-J. Cai**, Y. Wang, **R. Wanninkhof**, and H. Lüger (2008). Air-sea CO_2 fluxes on the US South Atlantic Bight: Spatial and temporal variability. *Journal of Geophysical Research-Oceans*, 113, C07019, doi:10.1029/2007JC004366.

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Reports:

Feely, R.A., and **C.L. Sabine** (2007). NACP West Coast Cruise report. http://www.pmel.noaa.gov/co2/wcccsw/

Peng, T. H., and **C. Langdon** (2007). The Gulf of Mexico and East Coast Carbon Cruise (GOMECC) cruise report. http://www.aoml.noaa.gov/ocd/gcc/GOMECC/CruiseReportfinal.pdf

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Special sessions at national conferences:

Cai, W., Jiang, L.-Q., Wang, Y., Hu, X., DeAlteris, J., Bauer, J., and Hopkinson C. (session chairs). Spatial and temporal variability of carbon dioxide signals and the biogeochemical controls in the South Atlantic Bight. Ocean Sciences Meeting (AGU), March 2–7, 2008. Orlando, FL.

Coble, P., and **S. Alin** (chairs). NACP/OCB Coastal Interim Synthesis Activities. Ocean Carbon and Biogeochemistry Summer Workshop, Jul. 2009.

McKinley, G., **S. Alin**, and J. Mathis (chairs). Carbon Cycling in the Coastal Oceans and Great Lakes, Ocean Sciences, Feb. 2009.

Wanninkhof, R., S. Alin, and D. Ianson (session chairs). Carbon Cycling in the Coastal Ocean. Fall American Geophysical Union meeting, Dec. 2008.

Presentations:

Alin, S., 2009. The North American Carbon Program (NACP) Coastal Interim Synthesis Activity: Carbon Synthesis Along North American Margins. Keynote presentation at the First Mexican Carbon Symposium, Ensenada, Mexico, Oct. 7–9, 2009.

Alin, S., J. Barth, A. Dickson, W. Evans, R. Feely, M. Goeckede, M. Goni, N. Gruber, B. Hales, M. Hernandez, D. Ianson, L. Juranek, B. Law, C. Maloy, J. Newton, G.-K.Plattner, C. Sabine, K. Shearman, P. Strutton, P. Tortell, V. Tunnicliffe, and A. Vander Woude, 2009. Recent (and Future) Advances in Carbon Cycle Synthesis along the North American Pacific

Coast. Plenary presentation at *North American Carbon Program 2nd All-Investigators Meeting* and *Ocean Carbon & Biogeochemistry Summer Workshop*.

Alin, S., A. Vander Woude, B. Hales, and P. Strutton, 2009. Seasonal evolution of carbon sources and sinks along the western continental margin of North America. Presented at *North American Carbon Program 2nd All-Investigators Meeting* and *Ocean Carbon & Biogeochemistry Summer Workshop*.

Alin, S.R., R.A. Feely, C.L. Sabine, G.C. Johnson, L.W. Juranek, A.G. Dickson, K. Lee, and A. Fassbender, 2008. Reconstructing aragonite saturation states along the California coastline using chemical and hydrographic data. *Eos Trans. AGU*, 89(53): Fall Meet. Suppl., Abstract OS53C-1328.

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Cai, W.-J., X. Guo, S.E. Lohrenz, F. Chen, and Y. Wang (Mar. 2007). Surface water CO_2 study in the Mississippi River Plume and Northern Gulf of Mexico. International SOLAS (Surface Ocean and Low Atmosphere Sciences) Open Science Conference, Xiamen, China,

Cai, W.-J. et al. Poster at the 2007 OCB summer meeting, Woods Hole.

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Cai, W. et al (contributed). Surface Ocean Alkalinity Distribution in the Western North Atlantic Ocean Margins. OS44A-08. Fall AGU (American Geophysical Union) meeting, 2008, San Francisco, CA.

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Feely, R.A., and C. Cosca (2007). Regional variability of seawater fCO_2 and sea surface temperature (SST) distributions along the Pacific West Coast between 32°N and 5°N. Joint Canada-U.S.-Mexico North American Carbon Program (NACP) PI meeting, Colorado Spring, CO (poster, breakout leader for two sessions).

Feely, R.A., **C.L. Sabine**, J.M. Hernandez-Ayon, D. Ianson, and **B. Hales** (2008). Evidence for upwelling of corrosive 'ocean acidified' water onto the continental shelf. Ocean Sciences Meeting, Orlando, FL.

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Feely, R.A., B. Hales, C. Sabine, D. Greeley, K. Lee, **S. Alin**, and L. Juranek, 2008. A new proxy method for estimating the aragonite saturation state of coastal waters using chemical and hydrographic data. *Eos Trans. AGU*, 89(53): Fall Meet. Suppl., Abstract OS33E-03.

Hales, B., (2007). Landscapes to coastal and oceanic carbon in the NACP. Joint Canada-U.S.-Mexico North American Carbon Program (NACP) PI meeting, Colorado Spring, CO.

Hales, B., **D. Feely**, **C. Sabine**, R. Letelier, P. Strutton, M. Saraceno, and T. Takahashi (2007). Improving predictions of coastal air-sea CO_2 fluxes, *Eos Trans. AGU*, 88(52) Fall Meet. Suppl., Abstract B41F-01.

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Sabine, C.L. (2007). Overview of proxy techniques for data extrapolation and interpolation. Surface Ocean pCO_2 Variability and Vulnerability Workshop, Paris, France, April 11-13 (invited talk).

Wanninkhof, R., **R.A. Feely, C. Langdon, J.-Z. Zhong, T.-H. Peng, C.L. Sabine, B. Hales**, **W.-J. Cai**, and **S.C. Hankin** (Jan. 2007). Coastal CO_2 measurements and databases for the North American Carbon Program: East Coast and Gulf Coast. Joint Canada-U.S.-Mexico North American Carbon Program (NACP) PI meeting, Colorado Spring, CO.

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7.0 Contacts

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